

March 1982

# Thermal and Oxidative Degradation Studies of Formulated C-Ethers by Gel-Permeation Chromatography

William R. Jones, Jr.,  
and Wilfredo Morales

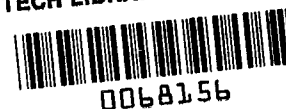


ALCOA COMPANY  
APRIL 1982  
MEMPHIS, TN

**NASA  
Technical  
Paper  
1994**

1982

TECH LIBRARY KAFB, NM



# Thermal and Oxidative Degradation Studies of Formulated C-Ethers by Gel-Permeation Chromatography

William R. Jones, Jr.,  
and Wilfredo Morales  
*Lewis Research Center  
Cleveland, Ohio*



National Aeronautics  
and Space Administration

Scientific and Technical  
Information Branch

## Summary

Gel-permeation chromatography has been used to analyze C-ether lubricant formulations from high-temperature bearing tests and from micro-oxidation tests. Three  $\mu$ -styragel columns (one 500 Å and two 100 Å) and a tetrahydrofuran mobile phase were found to adequately separate the C-ether degradation products. The micro-oxidation bench tests yielded degradation results qualitatively similar to those observed from the bearing tests. In general, microtests conducted in dry air revealed more degradation than did tests in dry nitrogen. However, there was no great difference in the thermal-oxidative stabilities of the two C-ether formulations, nor were there any differences in the catalytic degradation activities of silver and M-50 steel. C-ether formulation I (trifluoromethyl phenylphosphinic acid) did yield more high-molecular-weight products during a 111-hour bearing test than did C-ether formulation II (perfluoroglutaric acid plus phenylphosphinic acid) during a 25-hour bearing test.

A tentative degradation mechanism involving cleavage at the phenyl-sulfur or phenyl-oxygen bond, formation of radical intermediates, and a coupling of these intermediates with the parent molecules is proposed.

## Introduction

Advanced aircraft will place increased thermal stresses on lubricants and hydraulic fluids. Maximum fluid temperatures in excess of 316° C have been estimated for future applications (refs. 1 to 3). The C-ethers are a promising class of fluids for some of these applications (ref. 4). They have excellent thermal stability (390° C), good oxidation stability (260° C), and adequate pour points (−29° C). The main deficiencies of the C-ethers have been their poor boundary-lubricating ability and poor wetting characteristics (refs. 5 and 6). In addition, these fluids produce large quantities of a high-molecular-weight sludge under lubricating conditions (ref. 7). This sludge may degrade the boundary-lubricating properties and certainly reduces the useful life of the fluid.

Recently the development of high-pressure liquid chromatography has afforded a method for analyzing the degradation products of lubricants. Gel permeation is a form of liquid chromatography in which solute molecules

are separated according to size by permeation into a solvent-filled matrix (ref. 8). In addition, a sensitive micro-oxidation test has been developed at Pennsylvania State University (ref. 9) that reportedly simulates the conditions in a lubricating environment (ref. 10).

In this study two formulated C-ethers from high-temperature bearing tests were analyzed by using gel-permeation chromatography, and the results were compared with those obtained for the same fluids in micro-oxidation tests.

## Apparatus

### Liquid Chromatograph

A Waters model 244 liquid chromatograph was used. The unit was combined with an ultraviolet (UV) absorbance detector and a differential refractive index (RI) detector, or refractometer. The UV detector monitors the absorbance at a wavelength of 254 nm at sensitivities ranging from 0.005 to 2.0 absorbance units full scale (AUFS). The refractometer is sensitive to all compounds that differ in refractive index from the mobile phase. It will detect changes in the RI as small as  $10^{-7}$  RI units throughout the RI range 1.00 to 1.75.

i For these studies the liquid chromatograph was set up in the gel-permeation mode. One 500-Å and two 100-Å  $\mu$ -styragel columns were used. A schematic flow diagram of the liquid chromatography system is shown in figure 1. Gel permeation is a form of size-exclusion chromatography. Solute molecules are separated as a result of their permeation into a solvent-filled matrix in the column packing. This is schematically illustrated in figure 2. Here an idealized sample containing large and small molecules is shown passing through a gel-permeation column. The smaller molecules are able to penetrate into the pore structure of the gel, thus retarding their rate of travel through the column. The larger molecules are excluded and travel at a greater rate. Ideally, a complete separation will eventually be effected. In these studies tetrahydrofuran (THF) was the solvent at a flow rate of 1 milliliter/min. Figure 3 contains a calibration curve of log molecular weight as a function of column retention time for various standards. Retention time is defined as the time elapsed between sample injection and component detection as the sample elutes from the end of the column.

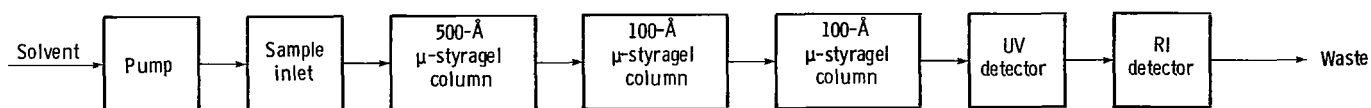


Figure 1. - Schematic flow diagram for liquid chromatograph.

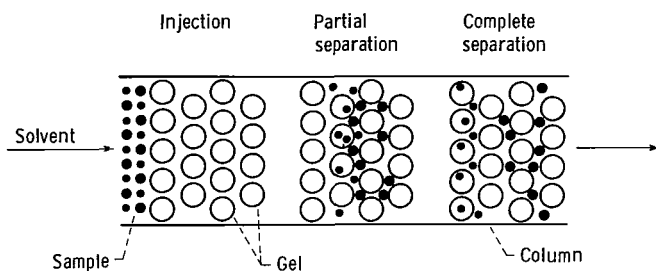


Figure 2. - Schematic diagram of gel-permeation chromatography.

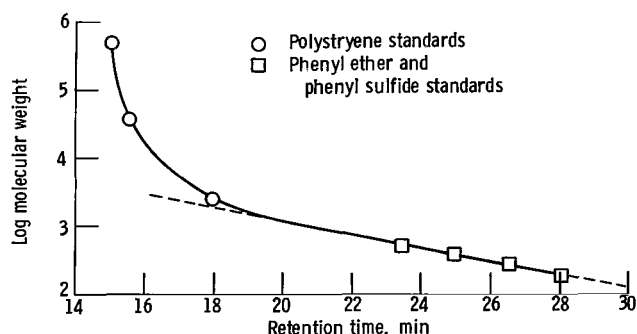


Figure 3. - Log molecular weight as a function of retention time for gel-permeation column set (one 500-Å and two 100-Å μ-styragel columns). Flow rate, 1 milliliter/min; solvent, tetrahydrofuran.

### Micro-Oxidation Apparatus

The micro-oxidation apparatus is illustrated in figure 4. This is essentially the oxidation apparatus developed at Pennsylvania State University (refs. 9 and 10). It consists of a glass tube fitted with an air entry tube. A catalyst specimen is placed at the bottom of the tube. The apparatus is located in a temperature-controlled oven. The two catalysts used were M-50 steel and silver.

### Bearing Test Apparatus

Both C-ether formulations were tested in full-scale, high-temperature bearing tests, and results and test details are reported in reference 11. These tests used 80-mm-bore bearings made of M-50 steel with silver-plated cages. Test conditions included a test duration of 100 hours, bearing speed of  $2 \times 10^6$  DN,  $260^\circ\text{C}$  oil inlet temperature, and  $316^\circ\text{C}$  outer race temperature, where DN denotes bearing bore (mm) times rotational speed (rpm).

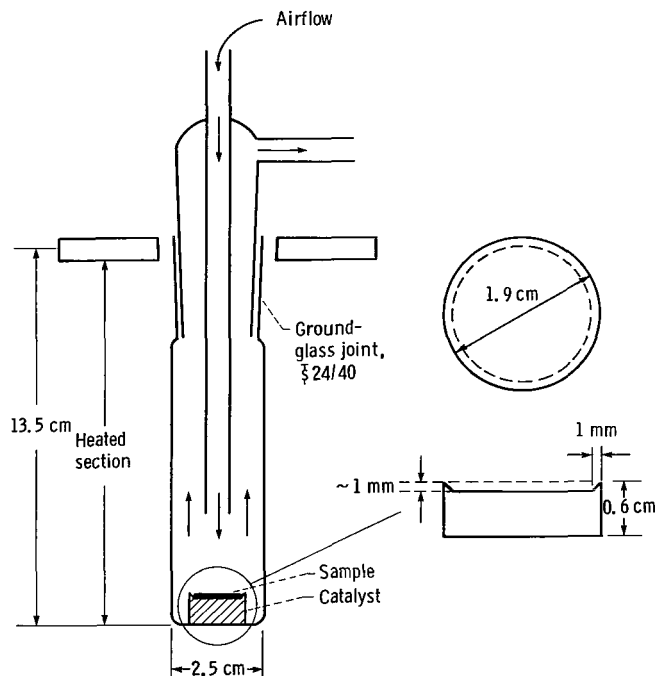


Figure 4. - Micro-oxidation apparatus.

## Test Procedure

The micro-oxidation apparatus with appropriate catalyst was placed in the oven and equilibrated to a temperature of  $353^\circ\text{C} \pm 1^\circ$ . A nitrogen flow rate of 20 milliliters/min was maintained during the equilibration period ( $\sim 30$  min). If the sample was to be tested in air, an air line was connected to the inlet tube 5 minutes before sample introduction. The nitrogen and air contained  $<20$  and  $<50$  ppm  $\text{H}_2\text{O}$ . A 100-microliter lubricant sample was introduced into the apparatus by removing the air line and inserting a long-stemmed syringe down the entry tube. After the sample was injected onto the top of the catalyst, the air line was reconnected and the test started. After 60 minutes the entire apparatus was removed from the oven and cooled in a stream of air. The air inlet was removed and 6 milliliters of tetrahydrofuran was added to dissolve the lubricant remaining on the catalyst. This solution was then filtered and was ready for analysis.

The liquid chromatograph was equilibrated at a flow rate of 1 milliliter/min for about 1 hour. Degassed and double-filtered THF (through a  $0.45\text{-}\mu\text{m}$  filter) was used. Then a 100-microliter sample from the lubricant-THF

solution was injected into the chromatograph. Total sample elution time (for all components) was approximately 30 minutes. Bearing test samples were analyzed directly in the chromatograph by dissolving 40 microliters of the used lubricant in 6 milliliters of the THF.

## Experimental Lubricants

The experimental fluids used in these experiments were a C-ether base fluid and three C-ether formulated fluids. These fluids are listed with their various additive contents in table I. Some typical properties of the C-ether base fluid are given in table II. The properties of each formulation were not measured, but because of their low additive concentrations, their values should not differ significantly from those for the base fluid. Finally, the chemical components of the base fluid are shown in figure 5. As can be seen, these fluids are blends of polyphenyl thioethers or mixed polyphenyl ether-thioether molecules. The exact concentration of each component is proprietary.

TABLE I. - EXPERIMENTAL FLUIDS

Fluid	Additive content	Concentration, wt %	Bearing test duration, <sup>a</sup> hr
C-ether base fluid	Dimethyl silicone	Proprietary	1
C-ether formulation I	m-trifluoromethyl-phenylphosphinic acid	0.075	111
C-ether formulation II	Perfluoroglutaric acid Phenylphosphinic acid	0.07 .06	25

<sup>a</sup>Ref. 11.

TABLE II. - TYPICAL PROPERTIES OF EXPERIMENTAL FLUIDS

[Manufacturer's data except where noted otherwise.]

Kinematic viscosity, m <sup>2</sup> /sec (cS), at -	
38° C .....	2.5 × 10 <sup>-5</sup> (25)
99° C .....	4.1 × 10 <sup>-6</sup> (4.1)
300° C .....	6.9 × 10 <sup>-7</sup> (0.69)
Pour point, °C .....	-29
Flashpoint, °C .....	230
Fire point, °C .....	285
Density at 38° C, kg/m <sup>3</sup> (g/milliliter) .....	1.18 (1.18 × 10 <sup>3</sup> )
Thermal decomposition (isoteniscope), °C .....	390
Vapor pressure at 371° C, torr .....	140
Surface tension at 23° C, N/cm (dynes/cm) .....	4.48 × 10 <sup>-4</sup> (44.8)

<sup>a</sup>Data from ref. 14.

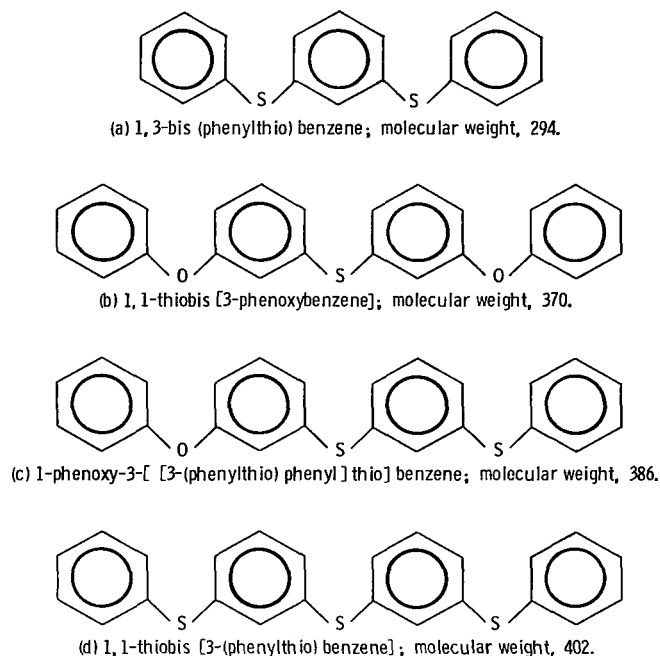


Figure 5. - Chemical components of C-ether base fluid.

## Results

### Base Fluid

A gel-permeation chromatogram of the unused C-ether base fluid taken with the refractive index detector is shown in figure 6. The mixture of three four-ring C-ether components is shown eluting first at an approximate molecular weight of 390. Essentially, two peaks are evident. The molecular weight scale was determined from the standard calibration curve (fig. 3). This mixture of four-ring components is not resolvable with the present system. The three-ring component eluted last at an

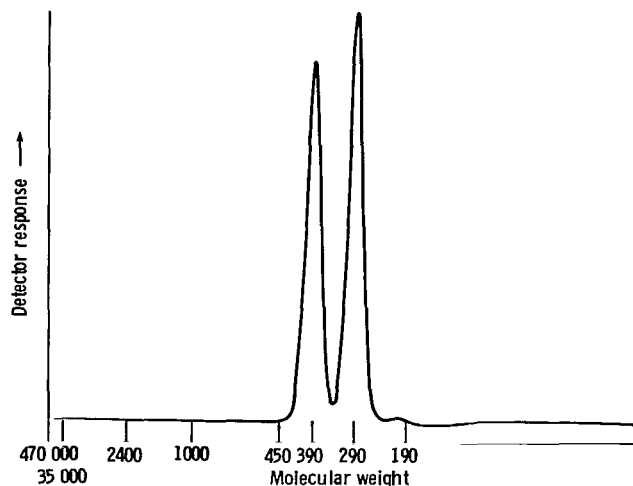


Figure 6. - Gel-permeation chromatogram for unused C-ether base fluid - RI detector (16X).

indicated molecular weight of about 290. A small amount (<1 percent) of lower-molecular-weight components was also present. The exact ratio of four-ring to three-ring components is not known with certainty. However, it appears to be about 1 to 1, or approximately a 50-percent mixture. The detector response is a function of the amount of material present and the difference between the refractive indices of the component and the carrier (THF). Therefore an absolute calibration would require a knowledge of the indices of all components as well as the percent distribution of four-ring compounds. Since these data are not available, all changes in chromatograms will be reported as relative changes based on peak area measurements. The area ratio of the three-ring components to that of the four-ring components is 1.17 for the unused fluid.

### Formulation I Bearing Test Samples

A chromatogram for formulation I, new and used, is shown in figure 7. In figure 7(a) (taken with the RI

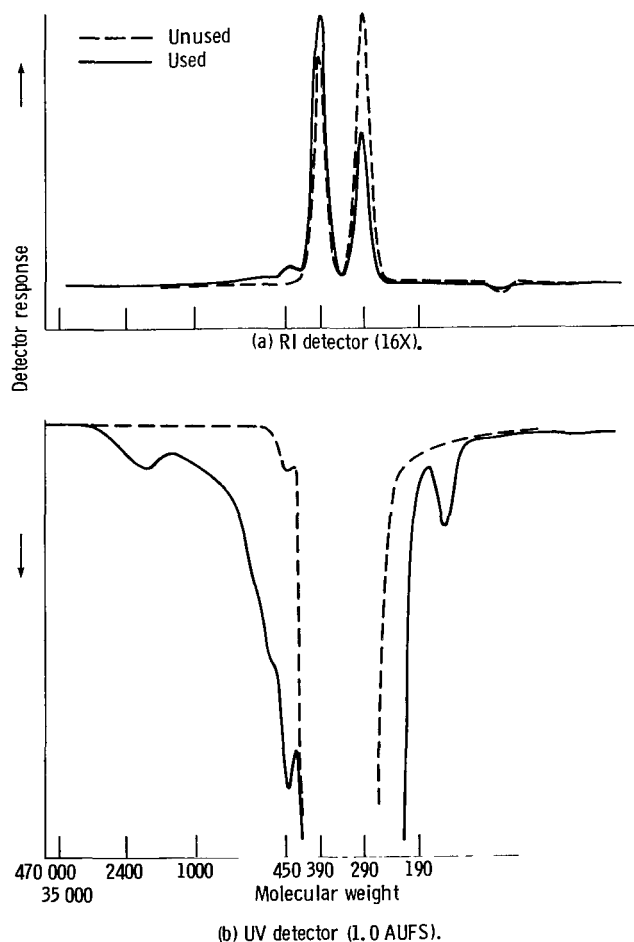


Figure 7. - Gel-permeation chromatogram for C-ether formulation I unused and from an 111-hr bearing test.

detector) there has been an obvious loss in the amount of the three-ring components and an apparent increase in the four-ring components. This is caused by preferential volatilization of the three-ring components. In addition, there is the appearance of higher molecular weight material, in the 400 to 1000 molecular weight range.

Figure 7(b) compares chromatograms of the new and used lubricants taken with the UV detector at 254 nm. Both high- and low-molecular-weight material is evident. A low-molecular-weight peak is present at about 140 to 150 and is thought to be associated with degradation products of the mobile phase (THF) since peaks often occur in this region when blank samples are injected. A high-molecular-weight peak is apparent at 450, two shoulders at 630 and 700, and a broad peak at 2400. The peak at 450 is also evident in the unused oil spectrum, but at much lower concentrations. It may be a five-membered ring compound (i.e., a five-ring polyphenyl ether has a molecular weight of 446).

### Micro-Oxidation Test Samples

The chromatograms from all of the micro-oxidation test samples indicate a lower sample concentration than the chromatograms of the bearing test samples. This difference is due to volatilization and/or degradation of the sample during the test. No attempt was made to recover all the condensed sample in the top of the apparatus or to trap volatile products from the exit tube. Therefore direct comparisons between chromatograms from the various oxidation tests is difficult.

**Air.** - Figure 8 shows the gel-permeation chromatography results for formulation I under standard conditions taken with a silver catalyst in dry air. Not much is evident in the RI trace (fig. 8(a)) but some higher molecular weight products appear in the UV chromatogram (fig. 8(b)). Again, there is a peak at 450 and a broad peak at 2400. A second broad peak is present at about 800. Qualitatively similar results for an M-50 catalyst are given in figure 9.

**Nitrogen.** - Analogous results for a nitrogen atmosphere are presented in figure 10 (Ag) and figure 11 (M-50). Three peaks of decreasing height appear in the RI trace (fig. 11(a)) at molecular weights of about 450, 600, and 700.

### Formulation II Bearing Test Samples

Results for new and used (25-hr bearing test) C-ether formulation II are given in figure 12. Data similar to those for formulation I (fig. 7) are evident but not as pronounced. Much less high-molecular-weight material (~1/3) is evident than for formulation I. Peaks occur in the UV trace (fig. 12(b)) at molecular weights of 450 and 600 but not at 2400.

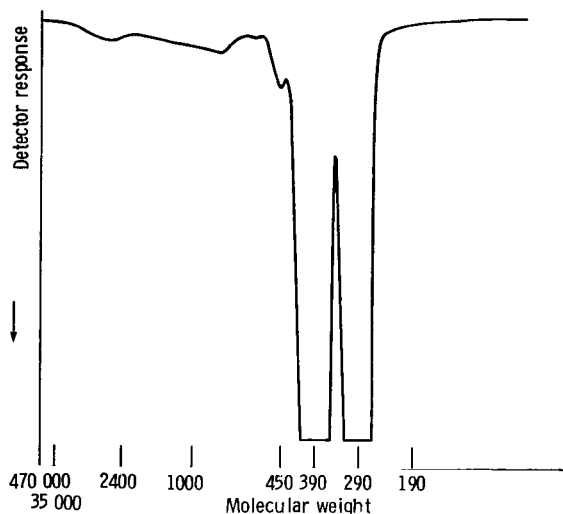
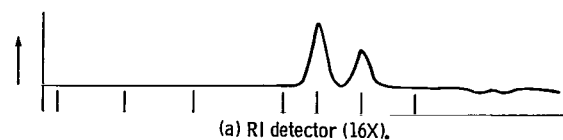


Figure 8. - Gel-permeation chromatogram of C-ether formulation I from micro-oxidation test (353°C, 60 min) - catalyst, silver; test atmosphere, dry air.

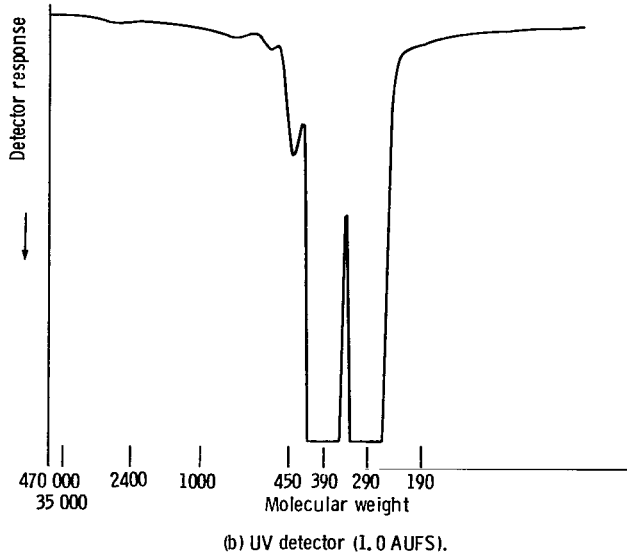
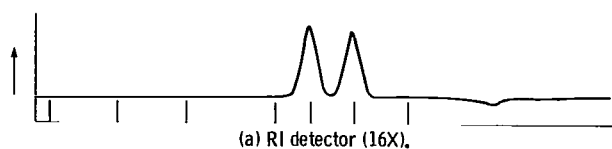


Figure 9. - Gel-permeation chromatogram of C-ether formulation I from micro-oxidation test (353°C, 60 min) - catalyst, M-50 steel; test atmosphere, dry air.

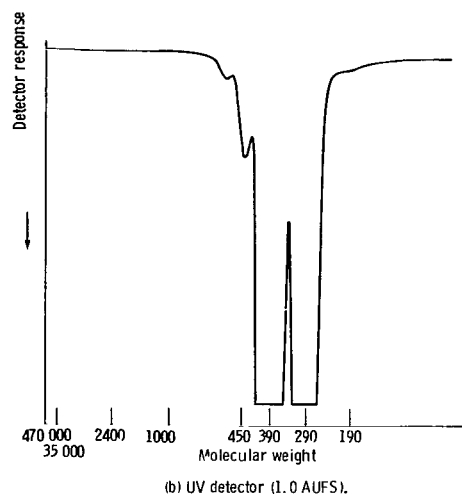
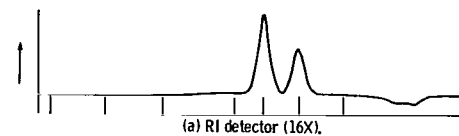


Figure 10. - Gel-permeation chromatogram for C-ether formulation I from micro-oxidation test (353°C, 60 min) - catalyst, silver; test atmosphere, dry nitrogen.

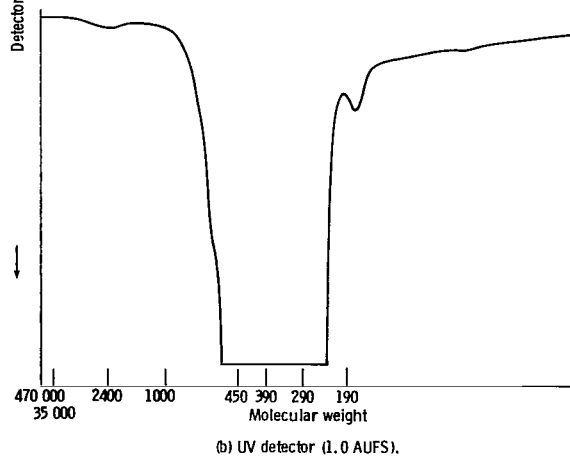
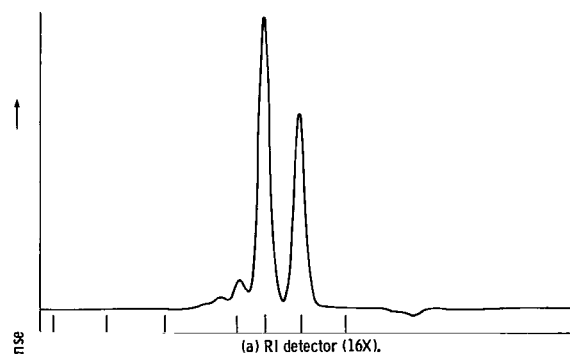


Figure 11. - Gel-permeation chromatogram of C-ether formulation I from micro-oxidation test (353°C, 60 min) - catalyst, M-50 steel; test atmosphere, dry nitrogen.

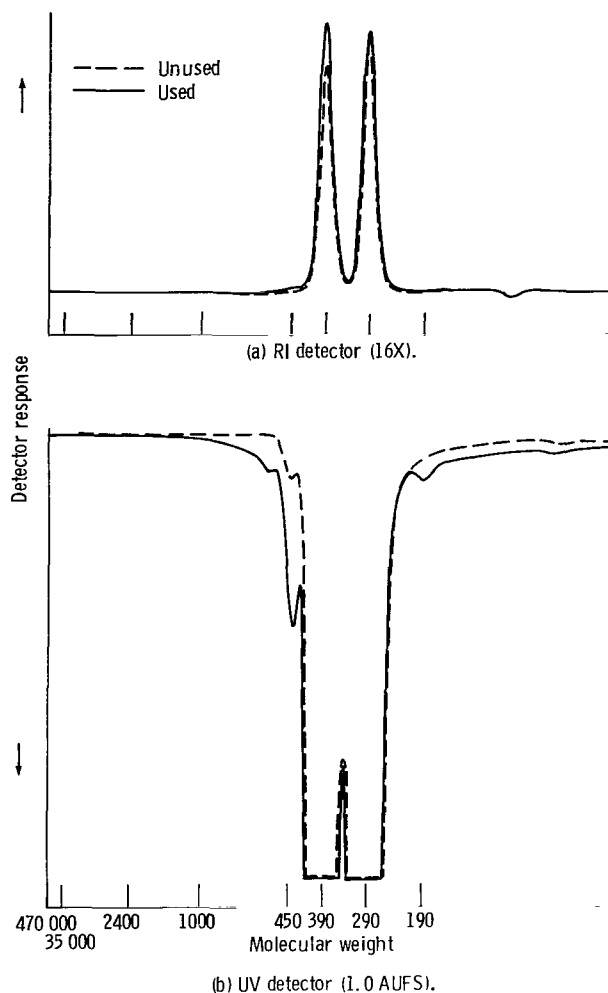


Figure 12. - Gel-permeation chromatogram for C-ether formulation II unused and from 25-hr bearing test.

### Micro-Oxidation Test Samples

**Air.** - Chromatograms for the silver catalyst are presented in figure 13. Two higher molecular weight peaks appear in the RI trace at 450 and 700. The UV trace yields peaks at 450 and 2400 with shoulders at 600 and 700. The M-50 data (fig. 14) show similar degradation products, but because of lower sample concentration the shoulders at 600 and 700 are better resolved.

**Nitrogen.** - Chromatograms for the silver catalyst are presented in figure 15. Figure 16 contains analogous data for the M-50 catalyst. Neither RI chromatogram shows much new material. However, both UV traces (figs. 15(b) and 16(b)) have peaks at 450 and 600. Figure 16(b) (M-50/UV) also has a small peak at about 900.

Differences in sample concentration have been evident in all of the micro-oxidation test samples. This is due to several factors. At the high temperature these tests were run at, 353° C, the base fluid is somewhat volatile. In

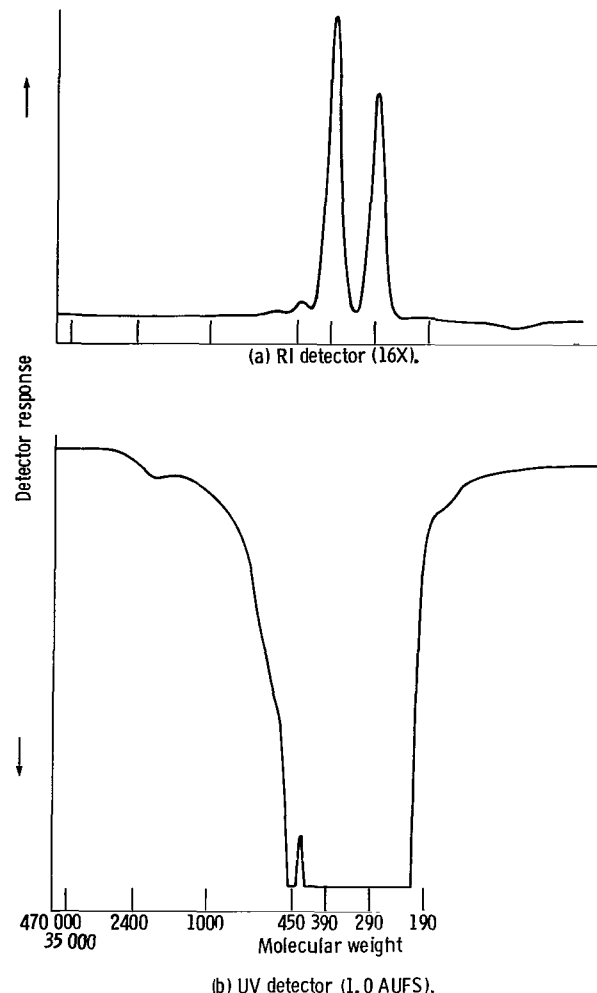


Figure 13. - Gel-permeation chromatogram of C-ether formulation II from micro-oxidation test (353° C, 60 min) - catalyst, silver; test atmosphere, dry air.

addition, under different test conditions, more volatile reaction products may be formed. And, finally, in order to optimize the concentration of high-molecular-weight degradation products, only lubricant remaining on the catalyst and near the bottom of the oxidation apparatus was dissolved in THF for analysis. Another problem is that all of the UV traces are off scale, due to very strong UV absorption by the phenyl rings. This persisted even at minimum UV detector sensitivity. Note that although the RI and UV traces are shown separately, samples were analyzed by both detectors at the same time.

Both of these problems make quantitative analysis of the degradation data difficult. However, even though there are concentration differences, the ratio of the parent three-ring C-ether components to the parent four-ring C-ether components can be determined from the RI data. These ratios are given in table III.

Comparison of the amount of degradation for the different tests is obviously impossible unless a sample concentration factor is taken into account. It was decided

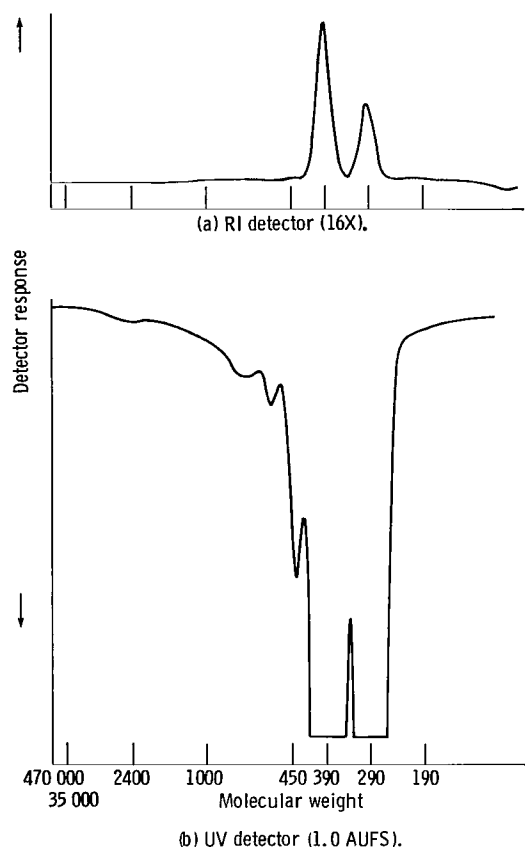


Figure 14. - Gel-permeation chromatogram of C-ether formulation II from micro-oxidation test - catalyst, M-50 steel; test atmosphere, dry air.

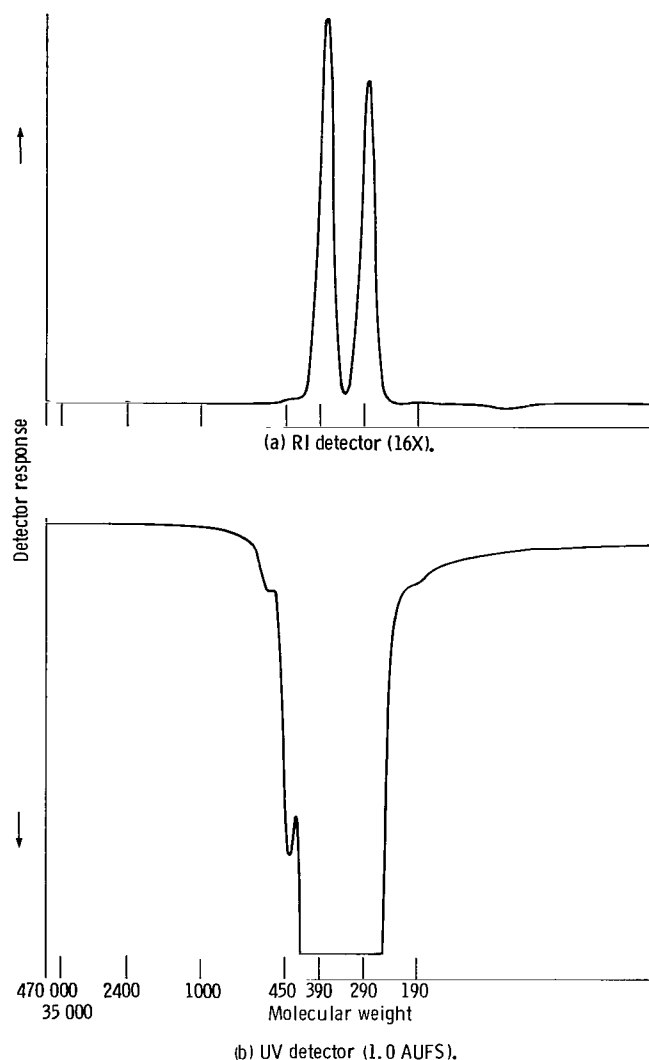


Figure 15. - Gel-permeation chromatograph for C-ether formulation I from micro-oxidation test - catalyst, silver; test atmosphere, dry nitrogen.

to use the amount of the C-ether four-ring components as a measure of sample concentration. The four-ring components are much less volatile than the three-ring components. It was realized that the four-ring components were also degraded and that possibly new four-ring components were formed during the tests. However, it was assumed that these changes were much smaller than the large changes in sample concentration. Therefore the areas under all of the four-ring-component peaks in the RI traces were measured with a planimeter. Then the peak areas under the higher molecular weight portion of the various chromatograms were similarly measured. The amount of high-molecular-weight material was then corrected on the basis of the concentration of the four-ring components in the RI trace. Because of the aforementioned problems in using the four-ring-component peak as the normalizing factor, only qualitative comparisons between the various parameters are reported. These comparisons are given in table IV.

TABLE III. - RATIO OF THREE- TO FOUR-RING COMPONENTS BY GEL-PERMEATION CHROMATOGRAPHY (RI DETECTOR)

	Formulation I	Formulation II
	Ratio of three- to four-ring components	
Unused	1.17	1.17
Micro-oxidation test samples:		
Ag catalyst, dry air	.49	.79
M-50 catalyst, dry air	.82	.49
Ag catalyst, dry N <sub>2</sub>	.43	.90
M-50 catalyst, dry N <sub>2</sub>	.67	.64
Bearing test samples:		
111 hr	.55	----
25 hr	----	.88

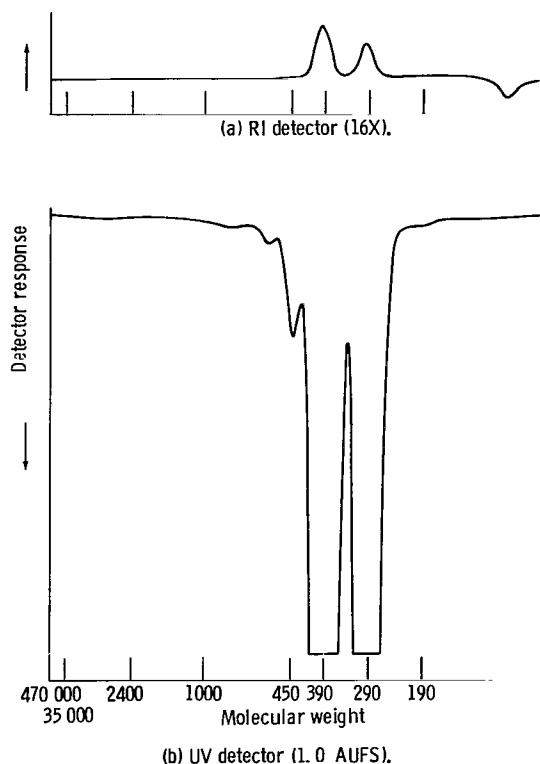


Figure 16. - Gel-permeation chromatogram of C-ether formulation II from micro-oxidation test (353° C, 60 min) - catalyst, M-50 steel; test atmosphere, dry nitrogen.

## Discussion

One of the objectives of this work was to develop a standard procedure for the use of gel-permeation chromatography to separate the various components of the C-ethers. As indicated by the data, this was accomplished by the use of only three  $\mu$ -styragel columns (one 500 Å and two 100 Å) and a THF flow rate of 1 milliliter/min. This allows for a complete analysis in less than 30 minutes. Better resolution can be obtained by adding more columns or decreasing flow rates but with a concomitant increase in analysis time.

### Formulation I Bearing Test Samples

Both C-ether formulations were tested in full-scale, high-temperature bearing tests; results and test details are reported in reference 11. These tests used 80-mm-bore bearings made of M-50 steel with silver-plated cages. Test conditions included a test duration of about 100 hours, bearing speed of  $2 \times 10^6$  DN, 260° C oil inlet temperature, and 316° C outer race temperature. Although formulation I ran 111 hours before rig shutdown, problems were encountered with this fluid including many filter pluggings, high bearing deposits, and some cage silver loss.

TABLE IV. - QUALITATIVE COMPARISON OF AMOUNTS OF HIGH-MOLECULAR-WEIGHT PRODUCTS FROM C-ETHER FORMULATIONS

[Amounts of high-molecular-weight products were corrected for differences in sample concentrations.]

(a) Comparison of formulations

Test conditions	Detector	
	Ultraviolet	Refractive index
Ag/air	I > II	II > I
M-50/air	II > I	I > II
Ag/N <sub>2</sub>	I > II	I > II
M-50/N <sub>2</sub>	II > I	I > II

(b) Comparison of test atmospheres

Catalyst	Formulation			
	I		II	
	Detector			
	Ultraviolet	Refractive index	Ultraviolet	Refractive index
Ag	Air > N <sub>2</sub>	N <sub>2</sub> > air	Air > N <sub>2</sub>	Air > N <sub>2</sub>
M-50	Air > N <sub>2</sub>	N <sub>2</sub> > air	Air > N <sub>2</sub>	Air ≅ N <sub>2</sub>

(c) Comparison of catalysts

Test atmosphere	Formulation			
	I		II	
	Detector			
	Ultraviolet	Refractive index	Ultraviolet	Refractive index
Air	Ag > M-50	M-50 > Ag	M-50 > Ag	Ag > M-50
N <sub>2</sub>	Ag > M-50	M-50 > Ag	M-50 > Ag	M-50 > Ag

Analyses of new and used samples of this fluid by gel-permeation chromatography were reported in reference 11. Ultraviolet chromatograms from that reference are reproduced in figure 17. Comparable chromatograms obtained in the present work are given in figure 7(b). The data from these two sources are essentially in agreement. The present data (fig. 7(b)), which were obtained with  $\mu$ -styragel columns, show more detail than the data from figure 17, which were obtained with less-efficient styragel

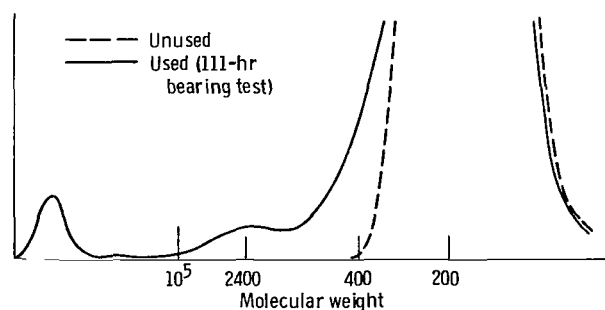


Figure 17. - Gel-permeation chromatograms for C-ether formulation I unused and from 111-hr bearing test. Attenuation, 16X; THF rate, 3 milliliters/min; UV detector. (From ref. 11.)

columns. Taking this into account, along with the low-molecular-weight (490) artifact in figure 7(b) and the high-molecular-weight ( $>10^5$ ) artifact in figure 17, the chromatograms are virtually identical. Both show an increase in the high-molecular-weight material region (400 to 35 000 in fig. 7(b) and 400 to  $10^5$  in fig. 17). The differences in the upper limits as well as in the lower molecular weight calibrations are due to the different columns and calibration standards used. Both show a substantial peak centered at about 2400 in the used-lubricant chromatogram.

### Formulation II Bearing Test Samples

Formulation II ran only 25 hours in the bearing test before failure occurred. Failure was attributed to overheating of both the bearing ( $393^\circ\text{C}$ ) and the oil ( $302^\circ\text{C}$ ). The gel-permeation chromatography data for this fluid are shown in figure 12. This fluid was not analyzed in reference 11. Degradation is less severe than for the formulation I bearing test sample. Formulation I yielded about four times the amount of high-molecular-weight products as did formulation II. The longer bearing test duration of formulation I may have been a factor. The UV chromatograms for the unused oil and bearing test sample (fig. 12(b)) indicate an increase in the 450-molecular-weight component and a small increase in the 600- to  $\sim 2000$ -molecular-weight range.

Comparing the bearing test samples (figs. 7(b) and 12(b)) with the UV chromatograms from the micro-oxidation tests suggests that similar degradative processes were occurring in both tests. The amounts of high-molecular-weight products and the appearance of certain high-molecular-weight peaks (i.e., 450, 500, and 2400) lend credence to the supposition that the micro-oxidation test simulates real-life conditions.

### Micro-Oxidation Test Samples

**Comparison of formulations.** - Table IV(a) contains the qualitative comparisons of the amounts of high-molecular-weight products for the various test conditions

and both detectors. The comparisons often differ depending on which detector is used. The RI detector is essentially an indiscriminate mass detector but much less sensitive than the UV detector. On the other hand, the UV detector only detects material that absorbs ultraviolet radiation at a wavelength of 254 nm. Therefore it is not surprising that they do not always agree. Taking this into account, there is no clearcut difference in the high-temperature stability (based on the generation of high-molecular-weight material) of the two C-ether formulations. This is not surprising when one considers that the formulations have identical basestocks and differ only in additive content. And these are boundary additives rather than oxidation inhibitors. However, it has been shown (ref. 12) that some boundary additives (e.g., tricresyl phosphate) that are known metal coaters can suppress catalytic degradation.

**Comparison of test atmospheres (air versus nitrogen).** - Table IV(b) contains comparisons between the different test atmospheres. Again, there are differences depending on detectors. However, with the exception of the RI data for formulation I the presence of oxygen increased the amount of degradation products. One would expect this result since most organic fluids degrade more rapidly in oxygen than in nitrogen. What is surprising is that the amount of air degradation products was not many times larger than the amount of nitrogen products. This would indicate that the thermal and oxidative processes are operating at similar rates at a test temperature of  $353^\circ\text{C}$  under catalytic conditions.

**Comparison of catalysts (silver versus M-50 steel).** - Table IV(c) contains comparisons between the catalysts. Again, no clear trend appears to exist. The variation of results would indicate that the catalytic activities of silver and M-50 steel in the tests were similar. This is in contrast to the data reported in reference 11, where silver produced 2 to 5 times the amount of high-molecular-weight degradation products as did M-50 under conditions essentially identical to those used in this work. The reason for this discrepancy is not known. Differences in catalyst surface chemistry may have been the cause. UV data for formulation I (from ref. 11) are presented in figure 18. Here a large peak at 2400 is evident for the silver catalyst. A smaller peak at 2400 and another peak at 400 appear in the steel data. However, the parent peak for the steel data is much lower than that for the silver data. If this is due to a difference in sample concentration, the statement that silver produces a greater quantity of high-molecular-weight products would not hold for this particular test.

One other point should be mentioned: The work of reference 11 used a low-carbon-steel catalyst rather than M-50 steel. However, the authors stated that in their experience low carbon steel yielded catalytic results similar to those for bearing steels.

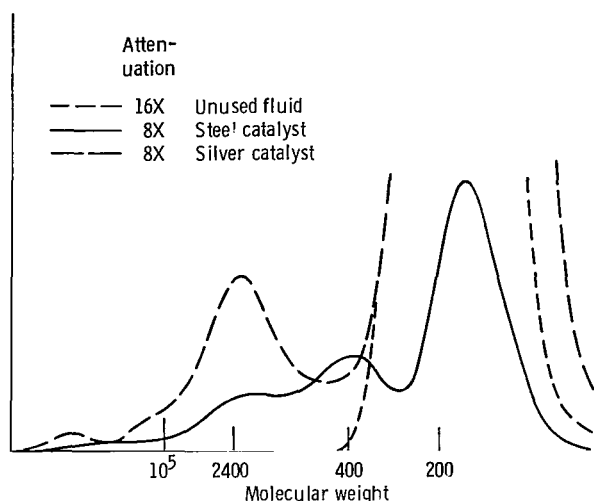


Figure 18. - Gel-permeation chromatograms for formulation I from micro-oxidation tests (353° C, 60 min). THF rate, 3 milliliters/min; UV detector. (From ref. 11.)

**Degradation mechanism.** - Classically, the degradation of polyphenyl ethers (which are structurally similar to the C-ethers) is thought to occur by attack of molecular oxygen at the phenyl-oxygen bond with the resulting symmetrical and asymmetrical cleavage forming phenoxy and peroxy radicals (ref. 13). These radical intermediates can undergo other reactions, but their termination step is a coupling reaction with the parent molecule. This then results in the formation of a series of higher molecular weight oligomers basically differing in molecular weight by the addition of another phenyl-oxygen species. A similar set of reactions could be written for the polyphenyl ether sulfur analogs (i.e., the C-ethers).

As mentioned in the results section, several discrete peaks of higher molecular weight were seen on many of the chromatograms from micro-oxidation tests in air. Peaks appeared at about 450, 600, 700, and 800 as well as the broad peak centered at 2400. It must be remembered that the gel-permeation chromatography calibration points are based on individual aromatic compound standards. In addition, the mechanism of separation is based on molecular size in THF and not molecular weight. Therefore the peak-molecular-weight assignments must be considered as rough values. Nevertheless it is compelling to resort to the previously described mechanism. Addition of a series of phenyl-sulfur moieties to a four-ring C-ether (thioether) would produce compounds having approximate molecular weights of 500, 600, 700, and 800, which compares very well with the observed results. However, the situation is not this simple. Similar peaks occurred in many of the dry nitrogen tests, where no oxygen was present. Apparently, a purely thermal process may also produce higher molecular weight homologs. Presumably the air

products would differ chemically from the nitrogen gas products. That is, oxygen should be structurally incorporated into these products. This can only be ascertained by isolating the products and characterizing them chemically, which is beyond the scope of this paper. At this point it is not understood why the high-molecular-weight peak at 2400 appears. This is definitely below the exclusion limit of the columns and is therefore not just a pile-up of very high-molecular-weight (but THF soluble) products. It could correspond to a condensation product of approximately 22 or 23 phenyl-sulfur moieties.

## Summary of Results

A gel-permeation chromatograph has been used to analyze C-ether formulations from bearing tests and from micro-oxidation tests. The major results are as follows:

1. The gel-permeation chromatograph using one 500-Å and two 100-Å  $\mu$ -styragel columns and a tetrahydrofuran mobile phase at a flow rate of 1 milliliter/min completely resolved the two major C-ether components and partially resolved higher molecular weight degradation products.
2. Qualitatively the micro-oxidation bench tests yielded degradation results similar to those observed from high-temperature bearing tests.
3. In general, micro-oxidation tests conducted in dry air produced greater quantities of high-molecular-weight products than did those tests conducted in dry nitrogen.
4. In general, there was not a great difference in the thermal-oxidative stabilities of C-ether formulations I and II as based on the generation of high-molecular-weight products in the micro-oxidation tests.
5. In general, silver and M-50 steel yielded similar catalytic activities as based on the generation of high-molecular-weight products in the micro-oxidation tests.
6. C-ether formulation I yielded more high-molecular-weight products during a 111-hour bearing test than did C-ether formulation II during a 25-hour bearing test.
7. A tentative degradation mechanism involving cleavage at the phenyl-sulfur bond, formations of radical intermediates, and a coupling of these intermediates with the parent molecules is proposed.

Lewis Research Center  
National Aeronautics and Space Administration  
Cleveland, Ohio, November 23, 1981

## References

1. Loomis, William R.; Townsend, Dennis P.; and Johnson, Robert L.: Lubricants for Inerted Lubrication Systems in Engines for Advanced Aircraft. NASA TN D-5420, 1969.
2. Zaretsky, Erwin V.; and Ludwig, Lawrence P.: Advancements in Bearings, Seals, and Lubricants. Aircraft Propulsion, NASA SP-259, 1971, pp. 421-463.
3. Sliney, Harold E.: Bearing, Lubricants, and Seals for the Space Shuttle. Space Transportation System Technology Symposium. III—Structures and Materials. NASA TM X-52876, vol. III, 1970, pp. 289-296.
4. McHugh, Kenneth L.; and Stark, Louis R.: Properties of a New Class of Polyaromatics for Use as High-Temperature Lubricants and Functional Fluids. ASLE Trans., vol. 9, no. 1, Jan. 1966, pp. 13-23.
5. Jones, William R., Jr.: Boundary Lubrication of Formulated C-Ethers in Air to 300° C. Lubr. Eng., vol. 32, no. 10, 1976, pp. 530-538.
6. Jones, William R., Jr.; and Hady, William F.: Effect of Humidity and a Wettability Additive on Polyphenyl Ether Boundary Lubrication of Steel in Air and Nitrogen to 350° C. NASA TN D-6055, 1970.
7. Jones, William R., Jr.: The Effect of Oxygen Concentration on the Boundary Lubricating Characteristics of a C-Ether and a Polyphenyl Ether to 300° C. Wear, vol. 73, no. 1, Nov. 1981, pp. 123-136.
8. Hamilton, R. J.; and Sewell, P. A.: Introduction to High Performance Liquid Chromatography. John Wiley & Sons, Inc., 1977.
9. Cvitkovic, E.; Klaus, E. E.; and Lockwood, F.: A Thin-Film Test for Measurement of the Oxidation and Evaporation of Ester-Type Lubricants. ASLE Trans., vol. 22, no. 4, 1979, pp. 395-401.
10. Lockwood, F. E.; and Klaus, E. E.: Ester Oxidation Under Simulated Boundary-Lubrication Conditions. ASLE Trans., vol. 24, no. 2, 1981, pp. 276-284.
11. Clark, F. S.; and Miller, D. R.: Formulation and Evaluation of C-Ether Fluids as Lubricants Useful to 260° C. (MRC-SL-1007, Monsanto Research Corp.; NASA Contract NAS3-19746.) NASA CR-159794, 1980.
12. Lockwood, F. E.; and Klaus, E. E.: Ester Oxidation—The Effect of an Iron Surface. Presented at the 36th Annual Meeting of the Amer. Soc. of Lubr. Engr., Pittsburgh, Pa., May 11-14, 1981. ASLE Preprint 81 AM 3D-2.
13. Wilson, G. R.; Smith, J. O.; and Sterniski, J. R.: Mechanism of Oxidation of Polyphenyl Ethers. ML TDR-64-98, Wright-Patterson AFB, Dec. 1963. (Available as AD-457120).
14. Jones, William R., Jr.; and Wedeven, Lavern D.: Surface-Tension Measurements in Air of Liquid Lubricants to 200° C by the Differential-Maximum Bubble-Pressure Technique. NASA TN D-6450, 1971.

1. Report No. NASA TP-1994		2. Government Accession No. -		3. Recipient's Catalog No.	
4. Title and Subtitle THERMAL AND OXIDATIVE DEGRADATION STUDIES OF FORMULATED C-ETHERS BY GEL-PERMEATION CHROMATOGRAPHY				5. Report Date March 1982	
				6. Performing Organization Code 505-32-42	
7. Author(s) William R. Jones, Jr., and Wilfredo Morales				8. Performing Organization Report No. E-976	
				10. Work Unit No.	
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135				11. Contract or Grant No.	
				13. Type of Report and Period Covered Technical Paper	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D. C. 20546				14. Sponsoring Agency Code	
15. Supplementary Notes					
16. Abstract Gel-permeation chromatography has been used to analyze C-ether lubricant formulations from high-temperature bearing tests and from micro-oxidation tests. Three $\mu$ -styragel columns (one 500 and two 100 Å) and a tetrahydrofuran mobile phase were found to adequately separate the C-ether degradation products. The micro-oxidation tests yielded degradation results qualitatively similar to those observed from the bearing tests. Micro-oxidation tests conducted in air yielded more degradation than did tests in nitrogen. No great differences were observed between the thermal-oxidative stabilities of the two C-ether formulations or between the catalytic degradation activities of silver and M-50 steel. C-ether formulation I did yield more degradation than did formulation II in 111- and 25-hour bearing tests, respectively.					
17. Key Words (Suggested by Author(s))  Thermal degradation Oxidation Ethers Chromatography			18. Distribution Statement  Unclassified - unlimited STAR Category 27		
19. Security Classif. (of this report)  Unclassified		20. Security Classif. (of this page)  Unclassified		22. Price*  A02	
				21. No. of Pages  13	

\* For sale by the National Technical Information Service, Springfield, Virginia 22161

National Aeronautics and  
Space Administration

Washington, D.C.  
20546

Official Business

Penalty for Private Use, \$300

SPECIAL FOURTH CLASS MAIL  
BOOK

Postage and Fees Paid  
National Aeronautics and  
Space Administration  
NASA-451



1 1 10,0, 031682 30090305  
DEPT OF THE AIR FORCE  
AF WEAPONS LABORATORY  
ATTN: TECHNICAL LIBRARY (SIL)  
KIRTLAND AFB NM 87117

**NASA**

POSTMASTER: If Undeliverable (Section 158  
Postal Manual) Do Not Return

---